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13. ABSTRACT (Maximum 200 words)  <p>New data for nitroalkanes support earlier results for nitroheterocycles indicating that C-NO<sub>2</sub> dissociation energies are related to the computed electrostatic potential maxima on the molecular surfaces above these bond regions. This presumably explains the well-established involvement of the electrostatic potential in impact sensitivity correlations; a second factor in the latter, for unsaturated systems, is the internal charge separation in the molecule.</p>				
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Relationships Between Dissociation Energies and Electrostatic Potentials  
of C-NO<sub>2</sub> Bonds: Applications to Impact Sensitivities

by

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## Introduction

An interesting feature of many C-NO<sub>2</sub> bonds is the presence of a buildup of positive electrostatic potential above the bond region. We observed this first in nitroaromatics [1-4], and subsequently in a variety of other unsaturated systems as well, including nitroheterocycles [5-8]. We have shown that these positive buildups can serve as initial sites for nucleophilic attack [2, 8].

A particularly intriguing aspect of the positive potentials associated with C-NO<sub>2</sub> bonds in unsaturated systems, and the focus of this paper, is their apparent relationship to the molecules' stabilities toward decomposition. We have become aware of this in the course of a continuing effort to learn how electronic and structural factors affect the sensitivities of energetic compounds toward shock and impact. The C-NO<sub>2</sub> grouping is of course a key component of many energetic molecules [9, 10], and the rupture of this bond is believed to often be a critical step in the decomposition process [11-18]. We are accordingly very interested in identifying factors related to the strength of the C-NO<sub>2</sub> bond.

In this paper, we shall review earlier evidence and present new data linking the positive electrostatic potentials above C-NO<sub>2</sub> bonds to their dissociation energies and to the sensitivities of the compounds. In this context, it is relevant to note recent work by March *et al*, in which density functional theory was used to show that a relation between dissociation energy and the electrostatic potential in the bond region is to be anticipated [19, 20].

## Molecular Electrostatic Potential

The electrostatic potential  $V(\mathbf{r})$  that is created in the space around a molecule by its nuclei and electrons is given rigorously by eq. (1):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

$Z_A$  is the charge on nucleus A, located at  $\mathbf{R}_A$ , and  $\rho(\mathbf{r})$  is the electronic density.  $V(\mathbf{r})$  is a real physical property, which can be determined experimentally as well as computationally [21]; it has been used extensively as a guide to molecular reactive behavior [21-25].

We have found it useful to compute  $V(\mathbf{r})$  on the surface of a molecule, which we define, following Bader *et al* [26], as the 0.001 au contour of the electronic density. The buildup of positive potential over a C-NO<sub>2</sub> bond then manifests itself as a local maximum in the surface potential, designated by  $V_{S,max}$ .

We have shown that a variety of macroscopic properties (including liquid, solution and solid phase) can be correlated and predicted by means of relationships involving statistically-defined quantities related to the surface electrostatic potential [27, 28]. These are properties that

reflect molecular interactions; e.g. solubilities [29-31], critical constants and boiling points [32], partition coefficients [33, 34], heats of vaporization and fusion [28, 35, 36], surface tension [36], liquid and crystal densities [36], and diffusion constants [37]. One of the statistical quantities that we use in these relationships is the average deviation of  $V(r)$  on the molecular surface,  $\Pi$ , given by eq. (2):

$$\Pi = \frac{1}{n} \sum_{i=1}^n |V(r_i) - \bar{V}_S| \quad (2)$$

$V(r_i)$  is the value of  $V(r)$  at point  $i$  on the surface, and  $\bar{V}_S$  is the average value of the potential on the surface. We interpret  $\Pi$  as a measure of the local polarity, or internal charge separation, that is present and may be very significant even in a molecule with zero dipole moment; for example, *p*-dinitrobenzene has considerable internal polarity and therefore a high value of  $\Pi$  [38], even though its dipole moment is zero due to symmetry. We have shown that  $\Pi$  is related to molecular polarity/polarizability and to dielectric constants [27, 38], and have found it to be effective in analytically representing various macroscopic properties [27, 28, 33, 34, 36].

### Sensitivity Relationships

Some time ago, in computational investigations of 1,3,5-trinitrobenzene derivatives [39, 40], we noted that the calculated charges on the carbon and nitrogen atoms of the C-NO<sub>2</sub> bonds were almost always both positive. While recognizing the ambiguity associated with the concept of atomic charge [24, 41-43], this observation was at least consistent with the buildup of positive potential over the C-NO<sub>2</sub> bond region (mentioned above) and also seemed likely to be a destabilizing feature of these bonds. Accordingly we investigated whether the electrostatic potential  $V_{\text{mid}}$  produced by the carbon and nitrogen charges at the bond midpoint, as given by eq. (3), might be a rough measure of relative bond strengths and therefore perhaps sensitivities [39, 40]. In eq. (3),

$$V_{\text{mid}} = \frac{Q_C}{0.5R} + \frac{Q_N}{0.5R} \quad (3)$$

$Q_C$  and  $Q_N$  are the atomic charges, which were obtained by the Mulliken population analysis procedure [44], and  $R$  is the C-N distance. Some justification for a possible correlation between  $V_{\text{mid}}$  and bond strength is given by Fliszár's formulation of bond energy in terms of atomic charges and the reciprocal of the internuclear distance [45, 46].

We found that there is indeed a rough linear relationship, for 1,3,5-trinitrobenzene derivatives, between  $V_{\text{mid}}$  values and measured impact sensitivities [39, 40]; the latter increase as

$V_{\text{mid}}$  becomes more positive. This is an additional indication of the significant role of C-NO<sub>2</sub> linkages in determining sensitivity, and focuses attention upon the electrostatic potential as a plausible property to investigate in this context. However any further interpretation of these results would be quite speculative, since it is not clear how physically meaningful is the quantity  $V_{\text{mid}}$ .

Recently we have approached this problem on a more rigorous level [47], using eq. (1) to compute *ab initio* HF/STO-5G electrostatic potentials on molecular surfaces. For the 1,3,5-trinitrobenzene derivatives **1** - **13** and the unsaturated nitroheterocycles **14** - **18**, treated separately, we found that the impact sensitivities could be well represented analytically in terms of the maxima of  $V(\mathbf{r})$  on the molecular surfaces,  $V_{S,\text{max}}$ , and the values of  $\Pi$ , reflecting the local polarity over each entire surface. The relationships are given below as eqs. (4) and (5) [47]:

1,3,5-Trinitrobenzene derivatives:

$$\text{Sensitivity}(h_{50}) = \alpha [\Pi^2 V_{S,\text{max}}(\text{ring})]^{-1} + \beta \Pi^2 + \gamma \quad (4)$$

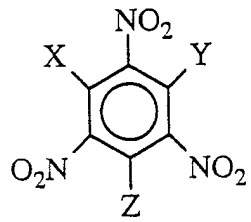
$$\alpha, \beta > 0; \gamma < 0; \text{linear correlation coefficient} = 0.989$$

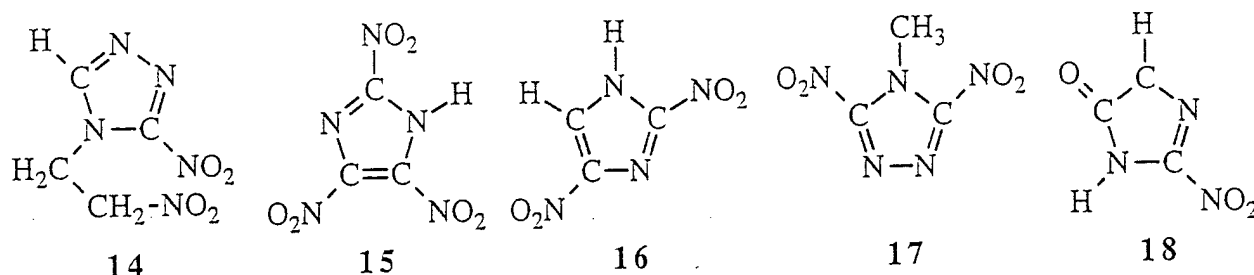
Nitroheterocycles:

$$\text{Sensitivity}(h_{50}) = \alpha [\Pi^2 V_{S,\text{max}}(\text{C}-\text{NO}_2)]^{-1} + \beta \quad (5)$$

$$\alpha > 0; \beta < 0; \text{linear correlation coefficient} = 0.986$$

The impact sensitivity is measured by the height,  $h_{50}$ , from which a given weight must be dropped on the material in order to produce detonation 50% of the time [9, 10]; the smaller is the magnitude of  $h_{50}$ , the greater is the sensitivity. In eq. (4),  $V_{S,\text{max}}(\text{ring})$  is the maximum of the surface potential above the aromatic ring; in eq. (5),  $V_{S,\text{max}}(\text{C}-\text{NO}_2)$  is the most positive of the maxima above the C-NO<sub>2</sub> bonds in the molecule.

	<u>X, Y, Z</u>	<u>X, Y, Z</u>
	1 CHO, H, H	8 CH <sub>3</sub> , H, H
	2 NO <sub>2</sub> , NH <sub>2</sub> , H	9 NH <sub>2</sub> , H, H
	3 CH <sub>2</sub> Cl, H, H	10 OC <sub>2</sub> H <sub>5</sub> , H, H
	4 Cl, H, H	11 OCH <sub>3</sub> , H, H
	5 OH, H, H	12 OCH <sub>3</sub> , OCH <sub>3</sub> , H
	6 H, H, H	13 NH <sub>2</sub> , NH <sub>2</sub> , H
	7 COOH, H, H	

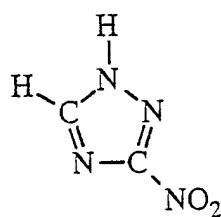


The trinitrobenzene derivatives do have surface potential maxima associated with the C-NO<sub>2</sub> bonds as well as above the ring [47]. The fact that the latter were found to be the more effective in relating to sensitivity may simply reflect the symmetrical arrangement of the nitro groups in these molecules; we do not view it as being necessarily inconsistent with the significance that has been inferred for the C-NO<sub>2</sub> regions.

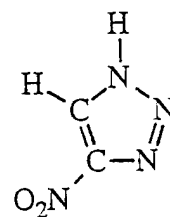
Eqs. (4) and (5) indicate that the impact sensitivities of the trinitrobenzenes and the nitroheterocycles are increased by the presence of strongly positive surface potential maxima and by high degrees of internal charge separation. Both of these effects are promoted by the strong electron-withdrawing powers of the nitro substituents, which counteract the stabilization through electron delocalization that is normally anticipated for unsaturated molecules such as are represented by eqs. (4) and (5). We have suggested that the extent of this destabilization, which is reflected in the  $V_{S,max}$  and  $\Pi$  values, may be a key factor in determining the sensitivity of each compound [47].

#### Dissociation Energies

In order to address directly the question as to how C-NO<sub>2</sub> bond strength affects sensitivity, we computed the C-NO<sub>2</sub> dissociation energies of the nitroheterocycles 15 - 17, 19 and 20, all of which have known impact sensitivities [48]. We used a nonlocal density functional procedure (GAUSSIAN 92/DFT [49], Becke exchange and Lee, Yang and Parr correlation functionals [50, 51], 6-31G\*\* basis set) which has been shown to give good results in such calculations [52-55]. Zero-point energies were taken into account.



19



20

No general relationship between sensitivity and C-NO<sub>2</sub> dissociation energy was found [48], although within pairs of molecules having the same ring structure (15, 16 and 17, 19), the impact sensitivity does increase as the strength of the C-NO<sub>2</sub> bond decreases. However we did find a definite correlation between the C-NO<sub>2</sub> dissociation energy and the maximum of the electrostatic potential above the bond. For the eight C-NO<sub>2</sub> bonds in this group of molecules, the trend is that the bond becomes weaker as  $V_{S,max}(C-NO_2)$  becomes more positive [48]. The linear correlation coefficient is 0.915, and it increases to 0.981 if one outlier is removed (the C-NO<sub>2</sub> bond between the two ring nitrogens in 16).

The existence of a relationship between the C-NO<sub>2</sub> dissociation energy and  $V_{S,max}(C-NO_2)$ , which is a function of the electronic density, is of considerable interest. It is consistent with the theoretical analysis by March *et al* [19, 20], and also provides insight into our earlier sensitivity correlations, as shall be discussed. Accordingly we present now the results of investigating its possible extension to another class of molecules, the nitroalkanes.

In Table 1 are listed experimentally-determined dissociation energies for the C-NO<sub>2</sub> bonds in eleven nitroalkanes, two of which also bear fluorines. For each of these molecules, we have computed  $V(r)$  on its surface at the *ab initio* HF/STO-5G//HF/STO-3G level [49]. Surface potential maxima were found to be associated with the C-NO<sub>2</sub> bonds, confirming that these are present in saturated as well as unsaturated molecules. These  $V_{S,max}(C-NO_2)$  values are also given in Table 1, along with the calculated surface areas.

It is clear that there is no general correlation between the C-NO<sub>2</sub> dissociation energy and  $V_{S,max}(C-NO_2)$  for these molecules. However one can be obtained if the surface area is taken into account. It is given by eq. (6), and shown in Figure 1.

$$\text{Dissociation energy} = 76.90 \left[ \frac{V_{S,max}(C-NO_2)}{\text{area}} \right] - 0.01119 [V_{S,max}(C-NO_2)]^2 + 43.42 \quad (6)$$

In eq. (6), the dissociation energy and  $V_{S,max}(C-NO_2)$  are in kcal/mole and the area is in Å<sup>2</sup>. The linear correlation coefficient for Figure 1 is 0.965 and the standard deviation is 1.92 kcal/mole.

### Discussion

The results that we have presented in this paper and earlier [48] are evidence of a link between the C-NO<sub>2</sub> bond dissociation energy and the electrostatic potential in the bonding region. The relationship involves other factors as well; one of these appears to be the size of the molecule. (The fact that this did not need to be taken into account for the nitroheterocycles [48] may simply indicate that the particular ones included in the study are similar in size.)

It now becomes easier to understand the continuing role of various forms of positive electrostatic potentials in analytical representations of impact sensitivity [39, 40, 47]. It seems

reasonable to infer that these positive potentials, e.g.  $V_{S,max}(C-NO_2)$ , are reflecting (inversely) the strengths of the C-NO<sub>2</sub> bonds. Thus we suggest that two key factors promoting impact sensitivity among trinitrobenzene derivatives and unsaturated nitroheterocycles are ease of C-NO<sub>2</sub> bond rupture and the counteracting (due to the NO<sub>2</sub> groups) of the stabilizing effects of charge delocalization. The first of these factors is represented in eqs. (4) and (5) by  $V_{S,max}$ , the second by  $\Pi$ .

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Figure Caption: Plot of predicted vs. experimental dissociation energies for the eleven nitroalkanes listed in Table 1. The linear correlation coefficient is 0.965.



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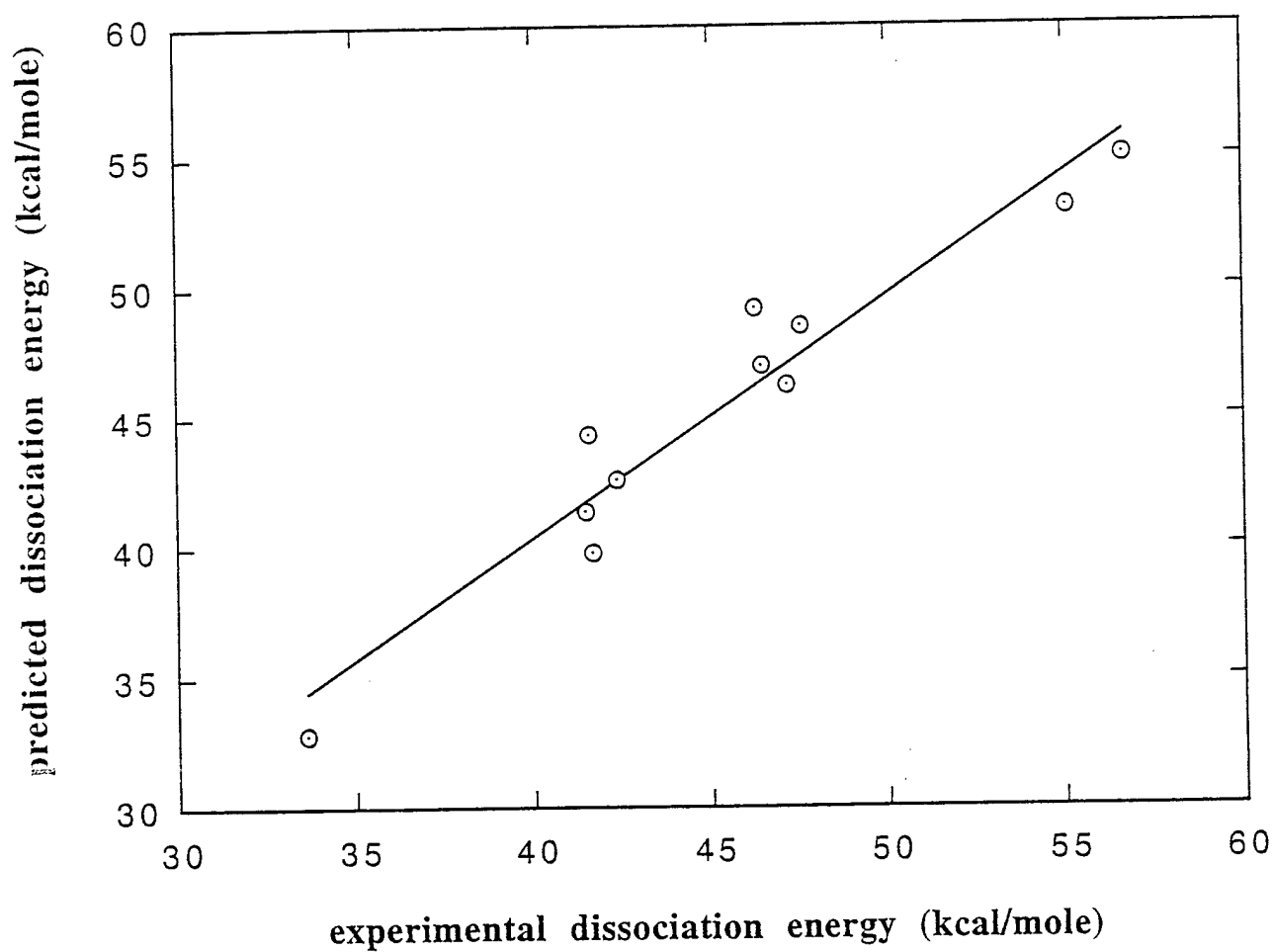
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Table 1. Nitroalkane properties.

Molecule	C-NO <sub>2</sub> dissociation energy, kcal/mole <sup>a</sup>	V <sub>S,max</sub> (C-NO <sub>2</sub> ), kcal/mole	Surface area, Å <sup>2</sup>
CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	56.67	24.2	102.5
CH <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	55.09	45.0	107.3
(CH <sub>3</sub> ) <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub>	47.56	36.0	141.2
CH <sub>3</sub> CH <sub>2</sub> CH(NO <sub>2</sub> ) <sub>2</sub>	47.16	41.8	143.8
CF <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	46.46	56.3	111.0
CH <sub>3</sub> CH(NO <sub>2</sub> ) <sub>2</sub>	46.27	43.0	125.0
CH <sub>3</sub> C(NO <sub>2</sub> ) <sub>3</sub>	42.35	48.9	145.0
CF(NO <sub>2</sub> ) <sub>3</sub>	41.66	58.0	131.4
CH(NO <sub>2</sub> ) <sub>3</sub>	41.56	51.8	128.8
CH <sub>3</sub> CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub>	41.47	46.5	161.6
C(NO <sub>2</sub> ) <sub>4</sub>	33.63	61.8	148.0

<sup>a</sup>G. M. Nazin and G. B. Manelis, Russ. Chem. Revs. 63 (1994) 313.



Plot of predicted vs. experimental dissociation energies for the eleven nitroalkanes listed in Table 1. The linear correlation coefficient is 0.965.